contain no H. Dawson[41] elucidated the X-ray crystal structure of the β isomer of $[P_2W_{18}O_{62}]^{6-}$ (Figure 2).

Removal of three WO_6 (or MoO_6) octahedra from a 12-heteropoly Keggin unit produces a 9-heteropoly "half-unit" (Figure 2). Two half-units join by sharing six O atoms to yield the 18-heteropoly structure. We have pointed out,[27] as a likely partial explanation of the α–β isomerism, that the two half-units may be joined in two ways: in one (the β isomer[41]) all of the atoms in one half-unit are eclipsed by corresponding atoms in the other half-unit (Figure 2); in the other form one half-unit is rotated 60° (around the axis through the P atoms) relative to the other, and reattached through sharing of the same O atoms, yielding a staggered arrangement for all the other atoms. This doubles the isomeric possibilities for the new 17-tungsto complexes. The data of Papaconstantinou and Pope[18,19,43] can be interpreted to show that the α isomers are 6-basic also, which negates VanDalen's suggestion[42] that the α isomer might consist of a combination of two half-units of a different sort, each formed by plucking one threefold edge-sharing tritungsto group from the Keggin structure. The latter arrangement would contain only 61 O atoms instead of 62 (because of sterically required O sharing between the central PO_4 tetrahedra) and so would be only 4-basic and not really an isomer. VanDalen's suggestion, however, may account for the third form sometimes reported.

Geometrical isomers (both 12-tungsto and 12-molybdo) of the Keggin structure also exist.[44–46] We suggest that these very possibly result from 60° rotations, about the threefold axes, of the trigonal edge-sharing W_3O_{13} (or Mo_3O_{13}) units of the Keggin structure and reattachment *via* sharing of the same O atoms. Five isomers for each formula are thus theoretically possible: the Keggin structure and the isomers wherein one, two, three, or all four of the trigonal units have been rotated.[47]

It is obvious that the geometrical isomers of the Keggin structure will probably yield numerous geometrical isomers for the new 11-heteropoly derivatives discussed in the beginning of this paper.

Further, the 18-tungsto structure (Figure 2) has, at its ends, two W_3O_{13} units, which can be rotated as we have proposed above for the 12-tungsto complexes from which the 18-tungsto anions are derived. *Each* of the (α and β) 18-tungsto isomers derived from 60° rotation of one 9-tungsto half-unit therefore also has the probability, if it is formed from the non-Keggin isomer of the 12-heteropoly derivative, of existing in up to three isomeric forms itself, yielding a total of six possible isomers for each 18-tungsto complex. Several combinations of these should be distinguishable by polarography.[49]

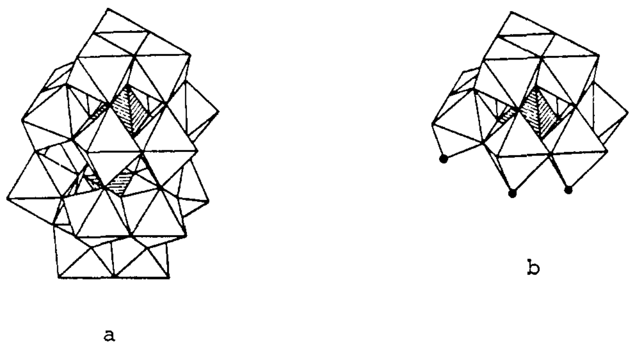

Figure 2. (a) The structure[41] of β-$[P_2W_{18}O_{62}]^{6-}$. A W atom is within each octahedron and a P atom is within each central tetrahedron. The centers of the O atoms are located by the vertices of the polyhedra. (b) The 9-tungsto (or 9-molybdo) "half-unit" (see text) formed by removal of three WO_6 (or MoO_6) octahedra from a 12-tungsto (or 12-molybdo) Keggin unit (Figure 1).

This situation also adds to the probabilities, already large as outlined above, for interesting geometrical isomerisms of the new 17-tungsto triheteroatom species. In fact it should be easier to distinguish and separate the isomers for certain of the 17-tungsto triheteroatom complexes than for the 18-tungsto anions, *via* a greater influence of the M^{m+} position on the properties.

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[43] E. Papaconstantinou, Ph.D. Dissertation, Georgetown University, 1968.

[44] W. Hückel, "Structural Chemistry of Inorganic Compounds," Vol. I, Elsevier, Amsterdam, 1950, p 183, and references therein.

[45] P. Souchay, "Polyanions et Polycations," Gauthier-Villars, Paris, 1963, p 62, and references therein.

[46] J. D. H. Strickland, *J. Amer. Chem. Soc.*, **74**, 868 (1952).

[47] The last possibility yields the structure once proposed by Kraus[48] for those 12-heteropoly ions for which Keggin[3] proved his well-known "Keggin structure."

[48] O. Kraus, *Z. Kristallogr.*, **91**, 402 (1935); **93**, 379 (1936).

[49] It is also probable that molybdo half-units can be made to combine with tungsto half-units, etc.

[50] Addressee for reprints and correspondence at Georgetown University.

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Hydrogen Scrambling in Organic Ions as a Function of Internal Energy. Extension of the Energy Range[1]

Sir:

The occurrence of H/D scrambling in organic ions in the mass spectrometer may considerably complicate the spectra of D-labeled compounds and consequently make conclusions hazardous in mechanism and/or structural studies. It would therefore be of considerable advantage to implement conditions under which such scrambling reactions are minimized. Variations in the degree of scrambling with ion lifetime (and hence with internal energy) have been observed in several cases,[2] and it is a common situation that a greater degree of scrambling is observed in metastable ions (low energy) compared with daughter ions formed in the source (higher energy) from the same reaction. This situation is a consequence of the lower appearance potential and the shallower rise of reaction rate constant, k, with ion internal energy, E (tighter activated complex), for the scrambling reaction compared with the decomposition reaction.[3,4] Therefore, in order to minimize scrambling reactions it should be desirable to develop means of investigating decompositions from higher energy molecular ions. This paper reports that secondary decompositions can provide information on molecular ions formed with a variety of internal

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[1] Metastable Ion Characteristics, XV; paper XIV: R. B. Fairweather and F. W. McLafferty, submitted for publication.

[2] See, for example, A. N. H. Yeo and D. H. Williams, *J. Amer. Chem. Soc.*, **91**, 3582 (1969).

[3] F. W. McLafferty and R. B. Fairweather, *ibid.*, **90**, 5915 (1968).

[4] D. H. Williams and R. G. Cooks, *Chem. Commun.*, 663 (1968).

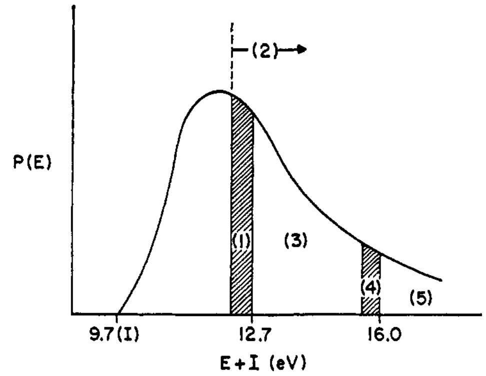

Figure 1. A hypothetical energy distribution in the benzoic acid molecular ion, showing the energy segments for formation of (1) unimolecular metastables, $M^+ \rightarrow M^+ - OH$; (2) collision-induced metastables $M^+ \rightarrow M^+ - OH$; (3) daughter ions, $M^+ - OH$; (4) metastable ions for loss of CO from $M^+ - OH$; and (5) daughter ions, $M^+ - OH - CO$.

energies including energies substantially higher than those observed with collision-induced metastables.[5]

A well-defined case of the variation of the degree of scrambling with internal energy is provided by deuterated benzoic acids.[6,7] Beynon, *et al.*,[6] have observed a ratio of 0.5 for the unimolecular metastable decompositions leading to $M^+ - OD$ and $M^+ - OH$, respectively, from the molecular ion of $C_6H_5CO_2D$, whereas in the corresponding daughter ions the $M^+ - OD$ ion is the more abundant. For benzoic acid, the narrow unimolecular metastable energy range will be around 12.7 eV (the appearance potential of the $M^+ - OH$ ion) and M^+ ions which form $M^+ - OH$ ions in the source have internal energy (relative to the neutral benzoic acid) between about 12.7 and 16.0 eV (further loss of CO to yield $M^+ - 45$ occurs above 16.0 eV).

Table I. Relative Losses of OD and OH as a Function of Internal Energy in Benzoic Acid O-*d*

Segment	Energy, eV	$\frac{M^+ - OD}{M^+ - OH}$	Ratio measured
1	~12.7	0.67 ± 0.07	$m^*(M^+ \rightarrow 105)/m^*(M^+ \rightarrow 106)$(uni)[a]
2	>12.7	0.96 ± 0.08	$m^*(M^+ \rightarrow 105)/m^*(M^+ \rightarrow 106)$(coll)[a,b]
3	12.7–16.0	2.9 ± 0.2	$[M^+ - OD]/[M^+ - OH]$[c,d]
4	~16.0	12 ± 2	$m^*(105 \rightarrow 77)/m^*(106 \rightarrow 78)$[d]
5	>16.0	>20	$[M^+ - CO_2D]/[M^+ - CO_2H]$[c,d]

[a] Defocused metastables for loss of OD, OH from M^+ (*m/e* 123). [b] $P = 2 \times 10^{-4}$ Torr. [c] Normal ions at the collector. [d] Corrected for ^{13}C.

Molecular ions which have sufficient energy to lose hydroxyl *and* to decompose by further loss of CO provide another energy range for study. The relative intensities of the metastables (defocused mode) for loss of CO from $C_6H_5CO^+$ and $C_6H_4DCO^+$ will represent the relative proportions of M^+ ions at an energy of about 16.0 eV which undergo the initial reaction *via* loss of OD and OH, respectively (neglecting secondary isotope effects). To carry the argument a step further, the relative intensities of the $C_6H_5^+$ and $C_6H_4D^+$ ions formed in the source represent the M^+ ions from still higher energy states which decompose *via* the respective pathways.

An energy range above that for unimolecular metastable formation can also be attained by collision of undecomposed molecular ions with neutral molecules.[5,8] Excitation to a higher electronic state is believed to occur,[8,9] and the resulting collision-induced metastables will show a degree of scrambling characteristic of the energy of the decomposing molecular ions.[10]

Five energy segments have thus been defined for which the relative extent of initial decomposition *via* loss of OD and OH may be investigated. These segments are represented schematically in Figure 1. In practice, of course, the energy cut-offs are not sharp. Experimental results for the five segments are shown in Table I. In the case of the collision-induced metastables (segment 2) the observed $m^*(M^+ \rightarrow C_7H_5O^+)/m^*(M^+ \rightarrow C_7H_4DO^+)$ ratio appears to indicate an energy region between about 13 and 14 eV.[10] The observed trend of an increased preference for loss of OD *vs.* loss of OH with increasing internal energy of M^+ is a clear indication of the more rapid increase of k for the direct bond cleavage in comparison to the increase in k for scrambling.

Benzoic acid provides a straightforward system for study since the initial decomposition involves no primary isotope effect (which would be expected to vary with energy), and the product ions used in the determinations even for segments 4 and 5 have lost only one H or D atom.

The decomposition of the toluene molecular ion ($C_7H_8\cdot^+ \rightarrow C_7H_7^+ + H$) is complicated by the possibility of a primary deuterium isotope effect, so both α-d_3- and ring-d_5-toluene were employed for the study of scrambling in this ion.[11] The secondary reaction $C_7H_7^+ \rightarrow C_5H_5^+ + C_2H_2$ used for investigation of segment 4 involves elimination of a hydrogen-containing neutral, so a summation technique has been adopted. For example, in α-d_3-toluene, the alternative primary decompositions lead to a multiplicity of secondary metastable decompositions. The ratio of the sum ($m_1^* + m_2^* + m_3^*$) of the three possible metastables (defocused mode) for loss of acetylene from $C_7H_4D_3^+$ to the sum ($m_4^* + m_5^* + m_6^*$) from $C_7H_5D_2^+$ will represent the relative

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(5) (a) W. F. Haddon and F. W. McLafferty, *J. Amer. Chem. Soc.*, **90**, 4745 (1968); (b) F. W. McLafferty and H. D. R. Schuddemage, *ibid.*, **91**, 1866 (1969).

(6) J. H. Beynon, B. E. Job, and A. E. Williams, *Z. Naturforsch. A*, **20**, 180 (1965).

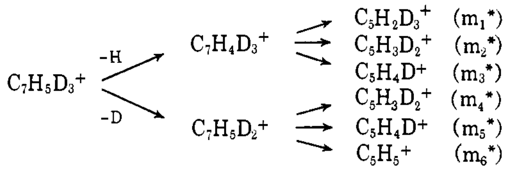
(7) S. Meyerson and J. L. Corbin, *J. Amer. Chem. Soc.*, **87**, 3045 (1965).

(8) F. W. McLafferty, I. Howe, R. Kornfeld, H. D. R. Schuddemage, and S.-C. Tsai, in preparation.

(9) T. F. Moran, F. C. Petty, and A. F. Hendrick, *J. Chem. Phys.*, **51**, 2112 (1969).

(10) Assuming that most of the molecular ions are unscrambled before collision, *i.e.*, the threshold for scrambling is not much lower than that for loss of hydroxyl.

(11) The toluene study in ref 5b assumed no change in the isotope effect.



proportions of M^+ ions at about 15.7 eV (the appearance potential of $C_5H_5^+$) which undergo the initial reaction *via* loss of H and D, respectively. Note that each of these metastable decompositions is uniquely determined in the defocused mode.

For the deuterated toluenes it is not possible to determine the decompositions from energy region 5 (*cf.* Table I and Figure 1) because of the overlap of the normal partially deuterated $C_5H_5^+$ ions formed from $C_7H_4D_3^+$ and $C_7H_5D_2^+$. For α-d_3-toluene the (loss of H):(loss of D) ratios for energy segments 1–4[12] are 4.7, 3.9, 1.8, and 1.0, respectively, and for ring-d_5-toluene the ratios are 1.7, 1.5, 1.1, and 1.6. The figures are influenced by (i) a deuterium isotope effect k_H/k_D which decreases with increasing energy[13] and (ii) scrambling *vs.* direct cleavage in the molecular ion. The fact that ratio 4 for ring-d_5-toluene is greater than ratio 3 is an indication of a decrease in the degree of scrambling (favoring H loss) with increasing energy despite a decrease in the isotope effect. In α-d_3-toluene both influencing factors will tend to increase the preference for loss of D with increasing energy. A detailed elucidation of the isotope effects and degree of scrambling in the toluene and cycloheptatriene systems will follow in the full paper.

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[12] Energy segments 1–4 are defined as for benzoic acid in Table I and Figure 1 except that the critical potentials become 11.8 and 15.7 eV instead of 12.7 and 16.0 eV.

[13] M. Vestal and G. Lerner, "Fundamental Studies Relating to the Radiation Chemistry of Small Organic Molecules," Aerospace Research Laboratory Report No. 67-0114, 1967.

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A Simple Molecular Orbital Explanation for the Barrier to Internal Rotation in Ethane and Other Molecules[1]

Sir:

Despite numerous calculations of barriers to internal rotation about single bonds,[2] a simple, qualitative explanation for the source of the barrier has failed to emerge. We here report a very simple explanation which applies to ethane at the independent-electron MO level and which is probably relevant at more sophisticated levels as well.[3]

The independent-electron, minimal basis set LCAO MO's for ethane are highly symmetry determined. The hydrogen 1s functions must enter in combinations characteristic of symmetry groups containing a C_3 axis. These are combined with C–C σ and π bonding and antibonding orbital combinations. The exact energy ordering of the MO's is dependent upon parameter choices, but reasonable choices within the extended Hückel MO (EHMO) method[4] indicate that the lowest seven MO's are C–H bonding, with C–C running through bonding and antibonding, leaving a net C–C σ bond. The highest seven MO's are C–H antibonding with C–C combinations producing a net σ antibond. Three of the seven filled MO's are nondegenerate and therefore contain hydrogen 1s functions in totally symmetric combinations (*i.e.*, all hydrogen 1s coefficients on a methyl group equal). These MO's suffer almost no energy change on going from eclipsed to staggered ethane. The other four filled MO's constitute two doubly degenerate sets, and contain the E-type methyl hydrogen symmetry combinations. These are the forms which are central to hyperconjugation arguments[5] and models,[6] and we shall see that their role in barrier production may be viewed in terms of a hyperconjugative extension to π orbital conformational arguments.[7] The lower energy pair of MO's is describable as C–C pseudo-π bonding, whereas the higher energy pair is C–C pseudo-π antibonding.[8] These MO's are sketched in Figure 1 for staggered and eclipsed ethane.

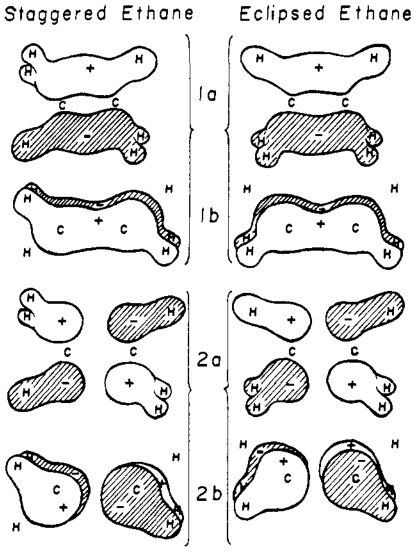

Figure 1. MO's of staggered and eclipsed ethane.

The levels **1** are lower in energy for the eclipsed form than for staggered. This MO stabilizes the eclipsed form by virtue of the bonding interaction between hydrogen 1s functions at opposite ends of the molecule. The levels **2** are lower in energy for the staggered form because the C–C π antibonding combination results in a sign change in the hydrogen coefficients at one end of the molecule. The energy change for levels 2 is the greater, the net effect giving a calculated barrier of

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[1] Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research.

[2] J. P. Lowe, *Progr. Phys. Org. Chem.* **6**, 1 (1968).

[3] J. A. Pople and D. P. Santry, *Mol. Phys.*, **7**, 269 (1963); **9**, 301 (1965); J. A. Pople and G. A. Segal, *J. Chem. Phys.*, **43**, S136 (1965).

[4] R. Hoffmann, *ibid.*, **39**, 1397 (1963).

[5] M. J. S. Dewar, "Hyperconjugation," Ronald Press, New York, N. Y., 1962, p 43.

[6] A. Streitwieser, Jr., "Molecular Orbital Theory," Wiley, New York, N. Y., 1961, p 131.

[7] R. Hoffmann and R. A. Olofson, *J. Amer. Chem. Soc.*, **88**, 943 (1966).

[8] The term "pseudo" is used here since we are not dealing with a planar system.